MEASUREMENT EQUIPMENT FOR MONITORING THE CHANGE OF NH₃ CONCENTRATIONS IN THE INDOOR ENVIRONMENT CAUSED BY TiO₂ PHOTOCATALYSIS

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Abstract
For monitoring the changes of ammonia and selected greenhouse gases concentrations in the indoor environment (e.g. stable environment) caused by TiO₂ photocatalysis was made the measurement equipment. The equipment consists of two identical parts, an area with photocatalytic TiO₂ and sources of radiation. Variable connection of these parts can be created a closed or an open path for air flow through the measurement equipment part. These two basic modes of measurement equipment allow measuring continuously the ammonia concentration by gas analyzer. The change of the air velocity passing through the measurement equipment allows managing contact time of air with photocatalytic TiO₂. The removable surface with photocatalytic TiO₂ is placed inside the equipment. The source of radiation is also removable - this allows changing the intensity of the radiation. The experiments with this measurement equipment were performed in a laboratory.

Keywords: Photocatalytic TiO₂, methane, air velocity, stable environment

1. INTRODUCTION
The report deals with the use of simple measurement equipment predominantly for laboratory experiments with testing of the influence of various kinds of affordable photocatalytic-active materials on harmful substances contained in the stables. These are in particular gaseous substances characterizing the state of stables and odour substances related to it up to a point. The following paragraphs present the results of measuring of the changes in concentration of selected gases in stables (NH₃, CH₄, N₂O) while using photoactive surfaces created from two kinds of affordable photocatalytic-active coats on the basis of TiO₂.

For the most photoactive substances, the positive influence of their application on the removal of organic and inorganic pollutants from the air is often stated. [1], [2] The air in stables is a result of a complex mixture of gases, including alcohols, aldehydes, amines, carboxylic acids, esters, ketones, organic sulfides, terpenes, aromatic compounds, hydrogen sulfide, ammonia, etc. [3] Its actual composition quite changes over the course of time, depending not only on the outside conditions (in particular atmospheric conditions and related regime of stable ventilation), but also on the inside conditions such as construction solution of the stable, used technical and technological systems and also the kind and category of the bred animals and their regime during 24 hours.

Therefore, we can assume that various kinds of photoactive coats will have different influence on the stable environment quality for various kinds and categories of animals and the way of their stabiling in the complex. The selection of a suitable kind of photoactive surface from the available selection directly for the given conditions based on progressive operational verification of photoactive coats would be demanding both concerning funding and time. Measurement equipment offers relatively quick and easy basic testing of the interaction of the air taken from the relevant stables with the given type of photoactive surface. This can be executed in lab conditions with air taken from the stables. Also, with regard to its dimensions, weight and undemanding operation (only source of electricity is necessary), the preparation can be transported to operational conditions. Concentrations of the monitored gases were secured by the air that was taken in the pig house. This environment for air samples in the first experiment was chosen due to the fact that pig houses show the highest potential for the use of photoactive coats due to its construction and the regime of
forced ventilation. Halls for chicken meat breeding are usually large scale so application of photoactive surface in the form of coat would be costly and it could be considered in smaller complexes only. Stables for cattle are ventilated naturally, so any application of technology improving the stable environment quality achieving greater effect would be complicated as well as objective measuring, and thus proving of those effects.

Measurement equipment should make the selection of the kind of photoactive surface that can be used for the improvement of stables much easier and help to decrease the negative influence of farming on the environment.

2. MATERIAL AND METHODS

All measurements were taken under laboratory conditions. For the purpose of monitoring the changes in the ammonia and selected greenhouse gases concentration in relation to the presence of photocatalytically active surface, measuring equipment has been constructed. It consists of two identical, physically separate and enclosed parts (experimental and referential), in which the air mass circulates (air with monitored gasses). Inside of both, the experimental and the referential part of the measuring equipment, an axial fan providing the air mass circulation, and a linear fluorescent lamp were placed. There is a carrier with the active surface positioned in the experimental part of the measuring equipment, and an identical carrier without this surface is positioned in the referential part.

Measuring equipment is assembled from the standard fittings of circular cross-section; the material is polypropylene with a smooth surface. The total weight of the device is 21 kg and each part has a volume of 0.04 m³. In the active zone of the experimental and the referential part of the equipment, a lamp and a carrier in the shape of a cylinder were always placed. The length of the active zone is 1.4 m, and the diameter of the fittings is 0.15 m. Gas analyzer probes were placed behind this active zone of the equipment, in the experimental and the referential part, always at the same place. By connecting of both parts of the equipment the original air flow trajectory around the surface can be doubled.

In the laboratory experiment, we tested two affordable photocatalytic-active surfaces. The first photocatalytic-active surface with working designation 1A was created by an aqueous suspension of photocatalytically active TiO₂ and inorganic binders from a Czech manufacturer. According to the manufacturer, this surface reduces the contents of organic and inorganic pollutants, bacteria, viruses, and other microorganisms in the air. The photoactive surface is activated by soft ultraviolet (UV-A) radiation which is part of sun radiation. The effectiveness of this surface in the pollutants reduction in the atmosphere is affected, inter alia, by the intensity of the UV radiation impact on the surface and by the airflow.

The photoactive surface was applied to the carrier in accordance with the manufacturer's instructions. Dispersion was first applied on one side of the carrier, then the interior paint, and then an aqueous suspension of TiO₂. The carrier for the referential part of the measurement device was treated only with dispersive interior paint. Second photocatalytic-active surface with working designation 1B was created using silicate coating composition with active photocatalytic on the basis of titanium dioxide. According to the information of the producer, the coating composition decomposes gaseous pollutant substances in the air and has a long-term antimicrobial and fungicide effect. Photocatalytic properties are activated by sunlight, i.e. UV radiation included in sunlight. To one side of the carrier, penetration was applied at first and then on the photoactive coat was applied. The carrier for the referential part of the preparation remained without photoactive surface.

In total, 8 carriers were created: Two carriers with photoactive surface 1A, two with photoactive surface 1B and four without the photoactive surface. Carriers with the photoactive surfaces were prepared according to the producers instructions for application. Carriers with photoactive surface 1A-1 and 1B-1 were permanently exposed in a pig house for six months prior to the experiment. The other two carriers with photoactive
surface designated as 1A-2 and 1B-2 and referential carriers were prepared prior to the respective phase of the lab experiment.

As the source of radiation, a commercially available linear fluorescent lamp with an electronic ballast with 30% UV-A and 5% UV-B, power of 8 W, length of 0.288 m, and the diameter of 0.016 m in diameter was used. The fluorescent lamp was attached using two simple hinges in the longitudinal axis of each part; in the middle of the active zone; the carrier was surrounding the lamp completely; the outer side of the carrier (not painted) followed the inner surface of the fitting. The circulation of air in experimental and referential part of the measuring equipment was ensured by axial fans of the same type, and velocity circulation was controlled by lockable slide valve located on the air intake to the fan.

As the source of NH₃, CH₄ and N₂O the air was taken from stables in a sample container of the volume 0.01 m³ with the sampling device. The air samples (including the monitored gases) were dosed at the same time to the experimental and referential part of the measuring equipment with vacuum pump. To each part of the measuring equipment, the air amounting to 0.001 m³ was dosed.

Continuous measurement of gas concentrations was carried out using the analyzer 1412 Photoacoustic Multi Gas Monitor with 1309 The Multipoint Sampler. The velocities of the air flow through the experimental and referential parts of the equipment were measured in accordance with CSN 12 4070 with an anemometer for low flow velocity measurements. In the experimental and the referential part of the equipment, the air temperature, relative humidity, pressure, and also the radiation intensity were monitored. All the measured data were analyzed using the Statistica 7.0. software.

3. RESULTS AND DISCUSSION

All values measured in the laboratory experiments were statistically processed. NH₃, N₂O and CH₄ concentrations of both parts of the measurement equipment were the main laboratory measurement outputs observed.

Photoactive surfaces 1A and 1B permanently exposed in stables for 6 months and photoactive surfaces prepared prior to the experiment (with the necessary advance for ripening) were tested. Testing of the impact of the selected surface on the NH₃ and also on CH₄ and N₂O concentration took place for 3 velocities (up to 0.5 m.s⁻¹, 1 m.s⁻¹, 2 m.s⁻¹) of air circulation around the surface. For each combination of surface and air circulation velocity up to 0.5 m.s⁻¹ (0.20 ± 0.04 m.s⁻¹, 0.32 ± 0.06 m.s⁻¹, 0.44 ± 0.06 m.s⁻¹), at least five repetitions were conducted (for 1 m.s⁻¹ and 2 m.s⁻¹ three repetitions). Experiments were focused on the monitoring of the influence of smaller velocities of ventilation up to 0.5 m.s⁻¹ in particular on the NH₃ and also on CH₄ and N₂O. Other monitored parameters (air temperature and radiation intensity) were constant during individual series of the tests. Individual measurements were performed using the same methods. The linear fluorescent tube with UV-A 30% and UV-B 5% was used as the source of light. Used fluorescent lamps and their setting in the measuring equipment were constant during the experiments, and therefore, it can influence the overall result only minimally except for the basic settings and their parameters.

The results of lab testing of the influence of two photoactive surfaces with working designations 1A and 1B on the concentration of NH₃, CH₄ and N₂O included in the air that was taken in the pig house (over the main source of these gases, i.e. feces) are stated in the following table (for velocities of ventilation up to 0.5 m.s⁻¹).
The results show decrease in the concentration of NH₃ and CH₄. Similar results were achieved during operational verification of effects of photoactive surfaces on the concentration of selected stable gases. [4], [5], [6], [7]. Concerning CH₄ at 1A, slightly quicker decrease was ascertained only in long-term period, on the other hand, concerning NH₃, the decrease is rather constant in the same period. The difference is very small. The achieved results show that at the circulation velocity of 1 m.s⁻¹ and 2 m.s⁻¹, as compared to the velocity up to 0.5 m.s⁻¹, the decrease of NH₃ and CH₄ concentration is only between 40 and 50% (and in long-term period – up to 1 hour) for photoactive surface 1A. 1B statistically showed insignificant differences (P ≤ 0.05) at higher circulation velocities (over 0.5 m.s⁻¹). Despite that, between the circulation velocities of 0.20 m.s⁻¹, 0.32 m.s⁻¹, 0.44 m.s⁻¹ statistically significant difference (P ≤ 0.05) in gas concentration between the test and reference part of the preparation was neither ascertained for 1A nor for 1B. The period of one passage of air through the whole preparation is, at the circulation velocity between 0.2 and 2 m.s⁻¹, from 117 to 11.7 s, and at lower velocities, the decrease of concentration for individual passages can be seen. In particular for 1A, it was obvious in the very first minutes of the measuring.

It is possible to observe, that the most decrease of NH₃ and in particular CH₄ concentrations was achieved at the circulation velocities of up to 0.5 m.s⁻¹ and for photoactive surface 1A. These circulation velocities often occur in stables, in the animals living zones (in the living zone, usually circulation velocities of up to 0.2 m.s⁻¹). In next zones (closer i.e. around the suction flaps), they can be higher. On the other hand, the corners of the complex may suffer from insufficient air circulation. The circulation velocities depend in particular on the ventilation regime in the complex and can thus change over the course of time. Lower ventilation velocities are achieved in particular during winter, during warmer periods, they can be a level higher, and particularly close to suction flaps they can reach values around 5 m.s⁻¹ in gusts; with the increasing distance from the flaps, they decrease.

The situation is somewhat different in the case of N₂O. The concentration of N₂O changes very little during the monitoring and it cannot be ascertained for sure that its concentration always decreases. In some cases, in particular in the case of 1A, a subtle increase of N₂O concentration was ascertained in the test part of the preparation as compared to the referential part. This can be, among other things, caused by partial decomposition of NH₃ at the presence of TiO₂ to N₂, N₂O or NO and H₂O. [8]

The conducted experiments also show that the content of water vapours in the air, in particular while its amount is unstable, was the cause of smaller efficiency of photocatalytic process, in particular at higher relative humidity for 1A. It was ascertained that air with relative humidity 40 – 50% shows more significant decrease of NH₃ and CH₄ compared to relative humidity 80 % and more. With 1B, this influence was not statistically significant (P ≤ 0.05).

During all executed partial experiments, no statistically significant (P ≤ 0.01) influence of the age of the photoactive surface on the achieved results, for 1A or 1B was ascertained.
During all experiments with 1A, subjectively, a significantly smaller intensity of odour in the test part compared to the reference part of it was ascertained. With 1B, this effect was not so unequivocal. Therefore, we plan to conduct objective monitoring of the odour substances using dynamic olfactometry in the future experiments.

The achieved results are not contradictory to the results of previous lab experiments [7], [9], where different setting of laboratory preparation was chosen. This preparation much better simulated the conditions in stable complexes. Its potential use in operational conditions in order to achieve a quick basic idea about the influence of the chosen photoactive surface on the monitored concentration of gases included in the environment of stables, i.e. stable microclimate, is limited by its construction solution and to achieve more precise results also by the necessity of long-term measuring (24 hours and more).

4. CONCLUSION

The objective of the work was to create and verify a simple measurement equipment for the execution of preliminary testing of photocatalytic-active surface (created by photocatalytic TiO₂ coatings) in order to decrease the concentration of selected gases and other pollutants in the environment of stables. The decrease of NH₃ has a provable positive effect on the yield of the cattle and also on the increase of the relation of the livestock production towards the environment by decreasing the emission of NH₃. With regard to the fact that the application of the stated photocatalytic coatings in stables requires investments (at least into adjustment – coating of the walls, and in case of insufficient sunshine also into illumination) it is vital to acquire at least basic information and knowledge concerning efficiency of this way of limiting the gas concentration prior to application. The selected setting of the measurement equipment allows quantifying, under laboratory conditions, the following:

- The influence of the photocatalytic-active surface on concentration of NH₃ and selected greenhouse gases.
- The influence of the kind of illumination necessary for the correct functioning of the photocatalytic-active surface.
- The influence of the velocity of ventilation on the changes of NH₃ and selected greenhouse gases concentration in time.

A certain level of error of the achieved results is caused, apart from other things, by the device itself, since it cannot imitate the actual conditions in the stable. These conditions vary in time and depend on many factors (from the setting of the stable with regard to cardinal points, through the kind and category of the cattle to atmospheric conditions). Therefore, it is possible that the selected photocatalytic-active surface generally showing positive effects during removal of pollutant substances from the air and decreasing its microbial contamination and odour can, even when all instructions of the producer for its maximum efficiency are maintained, show different results in various stable complexes than expected, i.e. achieved in lab and operational experiments. The described measuring equipment should provide basic information on the influence of the chosen photoactive surface.

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LITERATURE


